

CARDIVNSWC-TR- 61-98-16 Evaluation of Hydroxyethane Diphosphonic Acid (HEDPA) as Metal
Cleaning Agent Using Chemical and Electrochemical Test Methods: Part 1

Carderock Division
Naval Surface Warfare Center
West Bethesda, MD 20817-5700

CARDIVNSWC-TR- 61-98-16 June 1998

Survivability, Structures, and Materials Directorate
Technical Report

**Evaluation of Hydroxyethane
Diphosphonic Acid (HEDPA) as Metal
Cleaning Agent Using Chemical and
Electrochemical Test Methods: Part 1**

by

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19980916 028



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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 1998	3. REPORT TYPE AND DATES COVERED Research and Development	
4. TITLE AND SUBTITLE Evaluation of Hydroxyethane Diphosphonic Acid (HEDPA) as Metal Cleaning Agent Using Chemical and Electrochemical Test Methods: Part 1			5. FUNDING NUMBERS 98-1-6120-149	
6. AUTHOR(S) A. Srinivasa Rao and J. N. Murray				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Carderock Division Naval Surface Warfare Center Bethesda, MD 20817-5000			8. PERFORMING ORGANIZATION REPORT NUMBER TR-	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Naval Surface Warfare Center Carderock Division - ILIR Program West Bethesda, MD 20817			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Distribution unlimited. Approved for public release			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>In order to evaluate the adaptability of hydroxyethane diphosphonic acid (HEDPA) as an environmentally benign alternative rust removal agent, a systematic investigation is being carried out. The effectiveness of 2 vol.% (0.082 M) HEDPA was thoroughly investigated in the temperature range 27 – 60°C. The results suggest that the acid, HEDPA, is very effective in the rust removal process. It was found that the rust was completely removed by the HEDPA within 3 hours at 27°C, or within 30 minutes at 60°C. The rust dissolution process was found to have an activation energy of 11 ± 1 kcal/mole. Prolonged treatment of samples with HEDPA results in the re-deposition of the reaction products onto the cleaned sample surface. The reaction product appears to be a mixture of complex higher order iron phosphates.</p>				
14. SUBJECT TERMS Rust Removal, Chemical HEDPA, Reaction Kinetics, Electrochemical methods			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unclassified	

CONTENTS

	Page No.
FIGURES	ii
TABLES	iv
ABSTRACT	1
ADMINISTRATIVE INFORMATION	2
INTRODUCTION	2
THEORETICAL	7
EXPERIMENTAL	14
RESULTS AND DISCUSSION	17
SUMMARY AND CONCLUSION	39
ACKNOWLEDGEMENT	41
REFERENCES	42

FIGURES

	Page No
Figure1. The chemical structure of 1-hydroxy ethane-1,1 diphosphonic acid (HEDPA).	6
Figure 2. Schematic representation of typical rust removal process.....	10
Figure 3. Weight loss versus time plot of 3 different heavily rusted steel Samples in 2 vol % hydroxyethane diphosphonic acid solution at 27°C.	18
Figure 4. Weight loss versus time plot of 3 different heavily rusted steel samples in 2 vol % hydroxyethane diphosphonic acid solution at 40°C.	19
Figure 5. Weight loss versus time plot of 3 different heavily rusted steel samples in 2 vol % hydroxyethane diphosphonic acid solution at 50°C.	20
Figure 6. Weight loss versus time plot of 3 different heavily rusted steel samples in 2-vol % hydroxyethane diphosphonic acid solution at 60°C.	21
Figure 7. Weight loss versus time plot of heavily rusted steel sample in 2 vol % hydroxyethane diphosphonic acid solution at 27°C.	22
Figure 8. Visual characterization of sample surface and the solution phase during rust removal by 2 vol.% HEDPA at 27°C.	28
Figure 9. Typical x – ray diffraction obtained from cleaned steel sample that became coated with dark yellow precipitate (as a result of the re precipitation of reaction products) after 48 hours of chemical reaction with 2 vol.% HEDPA at 27°C.	29
Figure 10. Simplified Randles equivalent circuit model for metal – solution reactions.	32
Figure 11. Bode magnitude plots for steel – 2 vol. % HEDPA solution at 23°C as a function of exposure time.	33

FIGURES Cont.

Page No

Figure 12. Effect of 2 vol.% HEDPA on the double layer capacitance of steel surface as a function of continuing exposure time. 35

Figure 13. Time dependent changes to the pore resistance (R_{pore}) and R_p for steel during the steel sample surface exposure to 2 vol.% HEDPA at 23°C. ... 36

Figure 14. Calculated steel corrosion resistance ($\mu A cm^{-2}$) represented as a function of "free HEDPA" concentration at 23°C. 38

TABLES

Page No.

Table 1. Experimentally determined rate constants for rust removal from heavily rusted steel sample as a function of solution temperature. 23

Table 2. Time for the termination of accelerated rust removal and the corresponding chemical kinetic rate constants as a function of HEDPA solution temperature. 25

Table 3. Order of the chemical reaction for each stage of chemical transformation during rust removal of heavily rusted steel sample by 2 vol% HEDPA at different solution temperatures. 26

Table 4. Maximum time required for complete transition between different stages of chemical reaction represented as a function of solution temperature. . 30

Table 5. Corrosion rate versus exposure time as a function of stir number For steel samples immersed in 2 vol% HEDPA at 27°C. 40

ABSTRACT

In order to evaluate the adaptability of hydroxyethane diphosphonic acid (HEDPA) as an environmentally benign alternative rust removal agent, a systematic investigation is being carried out. The effectiveness of 2 vol.% (0.082 M) HEDPA was thoroughly investigated in the temperature range 27 – 60°C. The results suggest that the acid, HEDPA, is very effective in the rust removal process. It was found that the rust was completely removed by the HEDPA within 3 hours at 27°C, or within 30 minutes at 60°C. The rust dissolution process was found to have an activation energy of 11 ± 1 kcal/mole. Prolonged treatment of samples with HEDPA results in the re-deposition of the reaction products onto the cleaned sample surface. The reaction product appears to be a mixture of complex higher order iron phosphates.

ADMINISTRATIVE INFORMATION

This report covering the research work covering the period of FY 97 was funded by the CDNSWC Independent Research Program (ILIR), sponsored by the Office of the Naval Research, ONR 10, and administered by the Research Director, CDNSWC 0112, Dr. Bruce Douglas, under the program element 61152N, Task Area ZR-000-01-01 and the CDNSWC Work Unit 1-6120-149. This work was supervised within the Metals Department (Code 61) by Dr. L. F. Aprigliano (Code 612) and Mr. R. J. Ferrara (Code 613).

INTRODUCTION

The development of new materials with improved hot water and salt water corrosion resistance is very important. As these new materials are being proven, it is also important to develop procedures and methods to maintain the materials currently in use. Advanced maintenance processes would have applications in several areas, viz. the electric utility communities for the removal of deposits from the thermal power plant equipment, and in the civilian and military ship building industry where the removal of corrosion products from ship platforms, on-board tanks, etc. is necessary. Recent trends in the industrial and military sectors has been towards the acquisition of fewer new systems. Therefore, it is even more important to extend the operational life of the existing systems

The common classical rust and/or paint removal methods are based on the use of inorganic abrasive grits. This is changing to the use of organic grits or fine dry ice particles

and, most recently, to the use of high power water jet blasting to clean the surfaces. These procedures offer logistical advantages in the removal process, but the operational labor tends to be costly.

An alternative, less labor intensive approach would be to use an environmentally acceptable solution to dissolve the rust and paint within a reasonable period of time. This solution should be easily flushed from the surface resulting in an acceptable cleaned condition. Freshly cleaned surfaces would then require an additional preservation step in order to minimize new corrosion. The preservation is often done by applying an organic paint coating to the freshly cleaned surfaces. If the corrosion product removal by inferior chemical agents has left a chemical residue on the surface of the metal, the residue may weaken the metal - paint adhesion and bonding. Therefore, a technical challenge is to develop an environmentally acceptable recipe that removes the corrosion products from the existing aged surfaces without leaving a chemical residue harmful to the adhesive nature of the preservation coatings on the cleaned surface.

This project was undertaken to demonstrate cost effective alternative technology for the removal of the corrosion products in on-board ship tanks, on functional mechanical components, and on structural components while converting the corrosion product waste into an environmentally acceptable disposable waste. The technology was introduced to the NSWCCD by personnel from the Argonne National Laboratory (ANL) with an initial intent of providing a method for cleaning radioactive contaminated components. However, it was found that this technology can also be extended to remove conventionally contaminated (i.e. rusted) steel surfaces. Compared to the present mechanical cleaning systems, an

environmentally acceptable chemical cleaning system has the potential of reducing the ship maintenance costs. This cost benefit is the result of a shorter clean-up time, the accessibility afforded by liquids, and the environmentally acceptable disposability of the chemical reagents after the clean-up effort.

The overall program has two objectives: (1) to provide basic scientific information of the chemical and electrochemical interactions at the metal - chemical reagent interface during corrosion product removal by the chemical cleaning procedure, including a determination of the surface purity of the cleaned metal surface, and (2) to determine the adhesion and bonding characteristics of a protective organic coating applied to the cleaned steel surface. The specific technical tasks that will be addressed are :

- a). to follow and model the kinetics of the removal of corrosion products and characterize the microstructure and morphology of the cleaned surface,
- b). to coat the cleaned metal surface with an organic coating and study the adhesion and bonding characteristics, and
- c). to test the electrochemical and corrosion characteristics of the coatings in the laboratory using conventional chemical methods and the electrochemical impedance spectroscopy (EIS) technique.

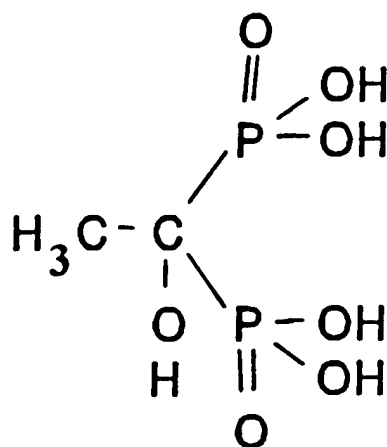
During the first phase of the investigation reported herein, the research effort was focussed on: (a) a determination of the classical chemical kinetic process parameters for the rust removal process as a function of solution concentration and the reaction temperature; (b) a characterization of the microstructure and morphology of the cleaned metal surface; (c) a

determination of the electrochemical characteristics of the metal-solution interface during the rust removal process using conventional and electrochemical impedance spectroscopy (EIS) techniques; and d) the modeling of the mechanism of the rust removal process in terms of the chemical kinetic and electro-chemical kinetic parameters.

In this first report, the results obtained for this new class of rust removing chelating agents will be presented following the chemical kinetic and electrochemical impedance spectroscopic study.

The reagent, 1-hydroxethane-1,1-diphosphonic acid, HEDPA, (also referred to as alkylphosphonic acid), is a water soluble liquid and has general physical characteristics similar to water. The chemical structure of the HEDPA is shown in Figure 1.

It can be noted from Figure 1 that the hydroxyethane diphosphonic acid has two phosphate groups and one extra hydroxyl (-OH) group. It is possible that the rust removal mechanism follows either the chemical reaction between the (-OH) and metal ion species and/or with the (P=O) cation sites and /or with the (P-OH) cation site. The collaborating researchers at the Argonne National Laboratory (ANL) using this chemical reagent have suggested that the chemical reaction products can be easily disposed because (a) the final reaction product is an EPA acceptable metal phosphate, and (b) the addition of commercial strength H_2O_2 will convert the HEDPA to CO_2 and the cation phosphate salt.



1-hydroxyethane-1,1 diphosphonic acid

HEDPA; C₂P₂ O₇H₈; MW = 206.02

Alkylphosphonic acid

IonQuest 201 (Albright & Wilson)

Figure 1. The chemical structure of 1-hydroxyethane-1,1 diphosphonic acid (HEDPA).

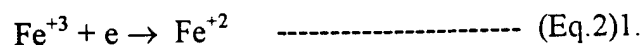
A series of publications by ANL personnel have described the kinetics of HEDPA interacting with synthesized pure isolated metal oxides [1-3]. Preliminary testing at ANL had suggested the oxide removal was selective and parent metal (steel) would not be attacked significantly by the acid. After the rust had been removed, a coating of various colors was noted on the steel surface. Phosphoric acid treatment of steel surfaces has been shown to improve the adherence of subsequently applied paint systems[4]. As the HEDPA is phosphorus based, the likelihood that the coating would serve in a similar fashion to a phosphated surface seemed possible. In that there are several potential applications for the use of this reagent, this preliminary investigation as to the relevance of cleaning steel was undertaken.

THEORETICAL

Two generally accepted mechanisms for the dissolution of metal oxides are reported in the literature [5-10]. The first is referred to as the adsorption mechanism [5,6] and the second is referred as the electrochemical theory [7-10]. Based on the electrochemical considerations it was suggested in the literature that the overall rate of dissolution of rust can be expressed as:

$$(d\alpha/dt) = k \{ (a_{H^+})^{0.5} (a_{Fe^{+2}})^{0.5} (a_{Fe^{+3}})^{-0.5} \} \text{ ----- (Eq.1)}$$

where "α" is the fraction of metal species dissolved, "a" the activity of acid, metal ion species and "k" the rate constant. For rust removal, the potential for the acid to dissolve iron species is determined by the reaction



From equations (1) and (2) it can be suggested that by lowering the $(\text{Fe}^{+3}/\text{Fe}^{+2})$ ratio, the rust removal process can be accelerated. If one assumes that the kinetics of the rust removal is a chemically controlled process, (i.e the rate limiting step is the surface reaction), the rate of rust removal can be expressed as [5-6]

$$[1 - \{1 - \alpha\}^{1/3}] = k't \quad \text{----- (Eq.3)}$$

where k' is the kinetic constant and t is the reaction time.

Although the above models can predict the dissolution kinetics of rust particles in HEDPA, the above models may not be applicable for predicting the rust dissolution off large surface area of rusted steel. In order to overcome the effect of large surface area on reaction kinetic modeling, a new model was developed. In this approach, it is assumed that the rust removal process proceeds as in a 2 - dimensional reaction. However, the reaction zone covers the entire surface area of the sample. The surface species first form a new and active nuclei which is dissolved by the HEDPA. The overall rate of rust removal can then be expressed as [7-10]

$$\ln[\alpha/(1-\alpha)] = k'' (t - t_i) \quad \text{----- (Eq.4)}$$

where k'' is the rate constant and ' t_i ' the time for the termination of the accelerated rust removal sequence.

In order to determine the chemical reaction rates of different processes involved in the rust removal, an alternative model was developed. This model is based on the assumption that the rust removal by hydroxyethane diphosphonic (HEDPA) acid is a solid state reaction process.

The overall (iron oxide dissolution) chemical reaction involves (a) removal of oxide (b) removal of pure metal; and (c) re-precipitation of metal complex. Therefore, it is justifiable to assume that the kinetics of the reaction process depends on both the acid concentration and the reaction temperature. Figure 2 shows a schematic representation of typical rust removal process in which several chemical activities may occur; such as the chemical reaction between (i) the sample oxide phase, (ii) both oxide and metal phase, (iii) only metal phase and possible adsorption of the reaction by product on to the metal surface, (iv) only the adsorption of reaction by product and or products and (v) the redissolution of the adsorbed precipitate and its re-adsorption.

A theoretical analog for the reaction kinetics process can be suggested as follows :
For convenience, assuming that only the first three phases are predominant during rust removal process by HEDPA acid, as the reaction progresses, the overall weight change with time can be represented as

$$(dW/dt) = - A \{ (dW_{oxide}/dt) + (dW_{metal}/dt) - (dW_{ppt}/dt) \} \quad (5)$$

where A = kinetic constant

(dW/dt) = rate of sample weight change

(dW_{oxide}/dt) = rate of oxide dissolved

(dW_{metal}/dt) = rate of metal dissolved and

(dW_{ppt}/dt) = rate of re-precipitation

An initial assumption is that the steel surface is “completely” covered by an oxide, i.e., no unoxidized iron is available for the chemical reaction. Once the rusted steel is exposed to the acid and the chemical reaction starts (reaction time $(t) = 0$) the HEDPA reacts only

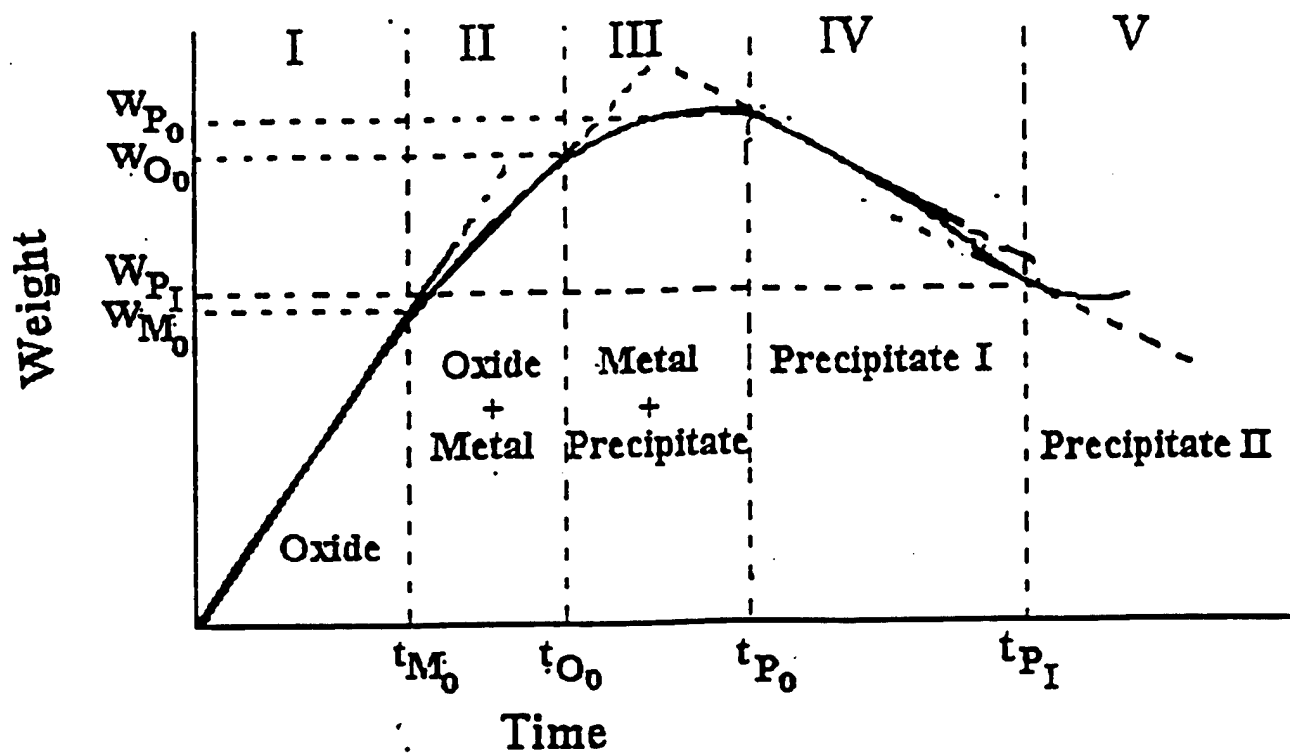


Figure 2. Schematic representation of typical rust removal process.

with the oxide layer (Region I). After certain time, the bare metal becomes exposed and, the acid interacts with both the metal and the decreasing quantity of oxide (Region II). Once a critical time is reached the dissolution process tends to be slow (Region III). At this stage, the re-precipitation of the reaction products onto the cleaned metal surface occurs and/or the reaction "by product" may form a complex with the acid in solution and even change the acid concentration (Region III).

Let, W_{O_0} , t_{O_0} be the weight change due to dissolution of metal and also re-precipitation of the reaction product (no oxide is present) and its corresponding time, W_{M_0} , t_{M_0} are the critical weight at which metal starts to dissolve and its corresponding time, W_{P_0} , t_{P_0} are critical weight at which no further metal is dissolved and its corresponding time, and W_{P_I} , t_{P_I} are the critical weight at which the initial precipitate starts to redissolve (perhaps due to the formation of new complex) and its corresponding time.

Since in the region I only rust is removed and the change in acid concentration depends upon the net weight loss of the rust, the generalized kinetic expression (Eq. 5) can be rewritten as

$$(dW/dt) = -A (dW_{oxide}/dt) \text{ and } (dW_{metal}/dt) \simeq (dW_{ppt}/dt) = 0 \quad (\text{Eq. 6})$$

Initially, the change in the acid concentration is small; therefore, the order of the overall chemical reaction with respect to the acid concentration can be approximated as zero order. The integral form of the rate process, then, can be expressed as

$$K_{R(I)}t = W + \text{Const.} \quad [\text{Limits : } t_0 \rightarrow t_{M_0}; 0 \rightarrow W_{m_0}]$$

$$k_O t = W + \text{Const.} \quad K_{R(I)} \simeq k_O \quad (\text{Eq. 7})$$

However, in region II, both the oxide and metal are being removed by the acid.

Therefore the order of the reaction with respect to the acid concentration can be approximated as a second order reaction

$$(dW/dt) = - A \{ (dW_{\text{oxide}}/dt) + (dW_{\text{Metal}}/dt) \} \quad (\text{Eq. 8})$$

and the integral form can be expressed as

$$k_{R(II)} = \{ W/W_o \} (W_o - W) \quad (\text{Eq. 9})$$

where W_o is the total weight of oxide and the metal removed in region II and

$$\text{and } k_{R(II)} t = \{ k_O \cdot W_{\text{oxide}} + k_M W_{\text{metal}} \};$$

$$W_{\text{oxide}} \simeq W_{\text{metal}} \simeq (1/2) \{ W_{O_o} + W_{M_o} \} \quad (\text{Eq. 10})$$

where W_{O_o} , W_{M_o} are the critical weights after which no oxide and metal was removed

$$k_{R(II)} t = [(1/2) \{ k_O + k_M \} \{ W_{O_o} + W_{M_o} \}] \quad (\text{Eq. 11})$$

In region III there is no oxide to be dissolved and the acid reaction takes place at the metal acid interface. In addition depending upon the conditions of the reaction, the reaction products are re-precipitated. When such a situation arises, the rate of weight loss can be represented as

$$(dW_{R(III)}/dt) = - A \{ (dW_{\text{metal}}/dt) - (dW_{\text{ppt}}/dt) \} \quad (\text{Eq. 12})$$

In region III also it can be approximated that with respect to the acid concentration, the order of the reaction is second order and integral form can be expressed as

$$k_{R(III)} t = \{ k_M W_{\text{metal}} - k_{\text{ppt}} \cdot W_{\text{ppt}} \} \quad (\text{Eq. 13})$$

If one assumes that in region III

$$W_{\text{oxide}} \simeq 0; \quad W_{\text{metal}} \simeq (1/2) \{W_{\text{O}_\text{O}} + W_{\text{P}_\text{O}}\} \text{ and } W_{\text{ppt}} \simeq (1/2) \{W_{\text{P}_\text{O}} + W_{\text{P}_\text{I}}\};$$

(where W_{P_O} and W_{P_I} are the critical weights at which neither oxide nor the metal is removed and the precipitate start forming respectively), the kinetic expression shown above (Eq. 13) can be rewritten as follows.

$$k_{\text{R(III)}} t = (1/2) \{k_{\text{M}} \{W_{\text{O}_\text{O}} + W_{\text{P}_\text{O}}\} - k_{\text{ppt}} \cdot \{W_{\text{P}_\text{O}} + W_{\text{P}_\text{I}}\} \quad (\text{Eq. 14})$$

The kinetic parameters for rust removal process thus can be determined as a function of both HEDPA concentration and reaction temperature. The above proposed model indicates that once most of the oxide (rust) is removed, the metal starts dissolving in the acid followed by the re-precipitation of the reaction products on to the surface of the cleaned surface. If one assumed that the rate of rust removal (Region I) is “ k_1 ” and the rate of metal and remaining rust removal (Region II) is “ k_2 ” and the re-precipitation (Region III) is “ k_3 ” respectively, it is possible to estimate the maximum time (t_{max}) required for the completion of each process (Region I – Region II – Region III) as follows:

$$k_1 \qquad k_2 \qquad k_3$$

Rust Sample \rightarrow Stage I \rightarrow Stage II \rightarrow Stage III

where, Stage I: Sample with Rust

Stage I – II : Sample with no rust and ppt formed

Stage I - II - III: Sample covered with thick Ppt. and/or Ppts.

The change in HEDPA concentration (C^*) can be represented as

$$C^* = C_{\text{stage I}} + C_{\text{stage II}} + C_{\text{stage III}} \quad (\text{Eq. 15})$$

Then the rate of change of acid concentration in each stage can be represented as

$$\text{Stage I} = - (dC_{\text{stage I}} / dt) = k_1 C_{\text{stage I}}$$

$$\text{Stage II} = - (dC_{\text{stage II}} / dt) = k_2 C_{\text{stage II}}$$

$$\text{Stage III} = (dC_{\text{stage III}} / dt) = k_3 C_{\text{stage III}}$$

where $C_{\text{stage I}}$, $C_{\text{stage II}}$ and $C_{\text{stage III}}$ are the acid concentrations at the corresponding stages.

Assuming that each stage process begins only after a maximum critical time (ie. the concentration function reaches a maximum and finally becomes "Zero"), the maximum time for the reaction process for Stage I - Stage II and Stage I - Stage II - Stage III can be expressed as

$$t_{\text{max (stage I - II)}} = [\ln (k_1 / k_2)] / (k_1 - k_2) \text{ and}$$

$$t_{\text{max (stage I-II-III)}} = [\ln (k_2 / k_3)] / (k_2 - k_3) \quad (\text{Eq. 16})$$

From the above equations (Eq. 15 and 16), it is then possible to predict the state of the chemical cleaning of the steel samples with HEDPA.

EXPERIMENTAL

Two types of conventional low carbon (1020) steel were investigated. Conventional epoxy mounted samples, polished to a 600 grit finish (SiC) for the electrochemical investigations were placed into the laboratory environment (ca. 25°C, 60% RH) for a minimum of two weeks prior to use. It is often assumed that the iron/steel when exposed to 60% RH condition at 25°C gets oxidized. The typical air formed oxide film thickness is believed to be few layers thick (~ 5 to 6 nm). Heavily rusted steel samples were prepared by suspending the steel panels from a fence adjacent to the NSWCCD Annapolis laboratory and the Severn River for a minimum of two weeks. The red rust content was approximately 30 mg/cm².

The commercial reagent Ionquest 201 (supplied by Albright and Wilson of Virginia) has 60 %w/o HEDPA; 40 wt.% water; and the solution specific gravity of 1.4 gm/cc and pH of 1.7. While the commercial Ionquest 201 was used for different applications, ANL scientists have identified the potential utility of Ionquest 201 for the dissolution of several metal ion species including iron. The present evaluation of the rust removal process was performed with a 2 v/o HEDPA stock solution made by diluting the as-procured commercial reagent. This concentration was selected based on earlier work at ANL and the pH of the 2 v/o solution was approximately 2.2 at 25°C.

Two types of experiments (weight change determination and electrochemical impedance spectroscopy (EIS) experiments) were performed. Sample weight changes with respect to increasing exposure times were used to evaluate the kinetics of oxide removal from the heavily rusted samples and subsequent formation of a new surface compound. Evaluations at four temperatures between 25 and 60°C were made to establish the kinetic parameters.

Electrochemical impedance spectroscopy (EIS) was utilized as the main electrochemical technique for monitoring the changes to lab- air formed oxide films on the smooth steel sample(s). The EIS technique involves the application of a small (usually ≤ 5 mV) ac voltage over a wide range of frequencies, typically for metal samples, 0.1 Hz to 10^5 Hz. The measured ac currents and phase shift values at the various frequencies are then examined and the various reaction and sample parameters can be derived from the data. The low frequency data can be used to identify the steel reaction kinetics whereas the intermediate frequency data indicate the steel surface "double layer capacitance" which can be related to the steel surface area. In the higher frequency range, one can determine the solution

resistance (therefore the conductivity and ionic concentration) and in this particular case, some characteristics of any impervious, non-conducting coating on the surface. The data have been analyzed for this effort using the simplified Randles equivalent circuit model as has been discussed elsewhere [12]. The EIS system utilized included the Princeton Applied Research (PAR) PARC Model 273 potentiostat, the EG&G 5206 Lock-in Amplifier with a conventional PC utilizing the PARC M388 software for system control and data accumulation.

The EIS experiments were conducted in conventional 800 cc open beakers with the approximately 500 cc solution stirred via a magnetically driven stirring bar. The steel piece to be tested was approximately 1.7 cm^2 , the edges and backside masked prior to the run by painting with MIL-P-24441 epoxy paint. A 0.25 inch diameter graphite rod served as the counter electrode and a conventional saturated calomel electrode (SCE) was used as reference. For the majority of the EIS runs, the stirring was turned off during the EIS run and resumed immediately after the completion of the EIS run. No attempt was made to control the solution temperature, which would increase from the initial value of 23°C to approximately 30°C within the first 8 hours. Usually some (20-30 cc) make-up deionized water was added after 48 hours of testing. The first four experiments were conducted with different liquid volume to sample area ratios. As the total 2 v/o HEDPA solution was kept approximately the same, the ratio was changed by suspending additional rusted steel pieces in the test solution. The fifth run was made using a 0.5 v/o HEDPA solution and a sixth run was made using 2 v/o HEDPA without any stirring to attempt to demonstrate a diffusionally controlled process via EIS.

RESULTS AND DISCUSSION

Figures 3-6 show typical weight change versus time profiles of rusted samples immersed in 2 v/o HEDPA solution and at different temperatures in the range 27 – 60°C. The solution volume to the sample exposed surface area ratio was maintained at approximately 25 cc/cm². The results shown in Figures 3-6 suggest that the rate of weight loss initially increases with time and once it reaches an optimum, the weight loss rate decreases and eventually tends to be zero. An increase in the solution temperature accelerates the reaction. At higher temperatures the weight loss versus time profiles show a weight gain due to re-precipitation of the products onto the sample surface.

The rate of reaction at different stages of the reaction process was then determined from the kinetic plots. The composite weight loss profile was later subdivided into sections and the critical transitions for different stages of the chemical reaction zones were identified. Figure 7 shows a typical weight loss versus time profile obtained from rusted samples subjected to the chemical cleaning by 2 vol% HEDPA at room temperature. The Stage I, Stage II and Stage III relate to the chemical reaction zones where only oxide was dissolved, some oxide and mostly metal was dissolved and some metal was dissolved and the reaction products were predominantly re-precipitated. The overall rate of reaction was determined by obtaining the slope with best fit of the weight change versus time profile. Table 1 shows the estimated rate constant values for rust removal as a function of temperature. From the overall reaction rate constants, the activation energy for the rust removal by 2 vol.% HEDPA was determined. It was found that this reaction rate process is associated with an energy of activation of 11 ± 1 kcal/mole.

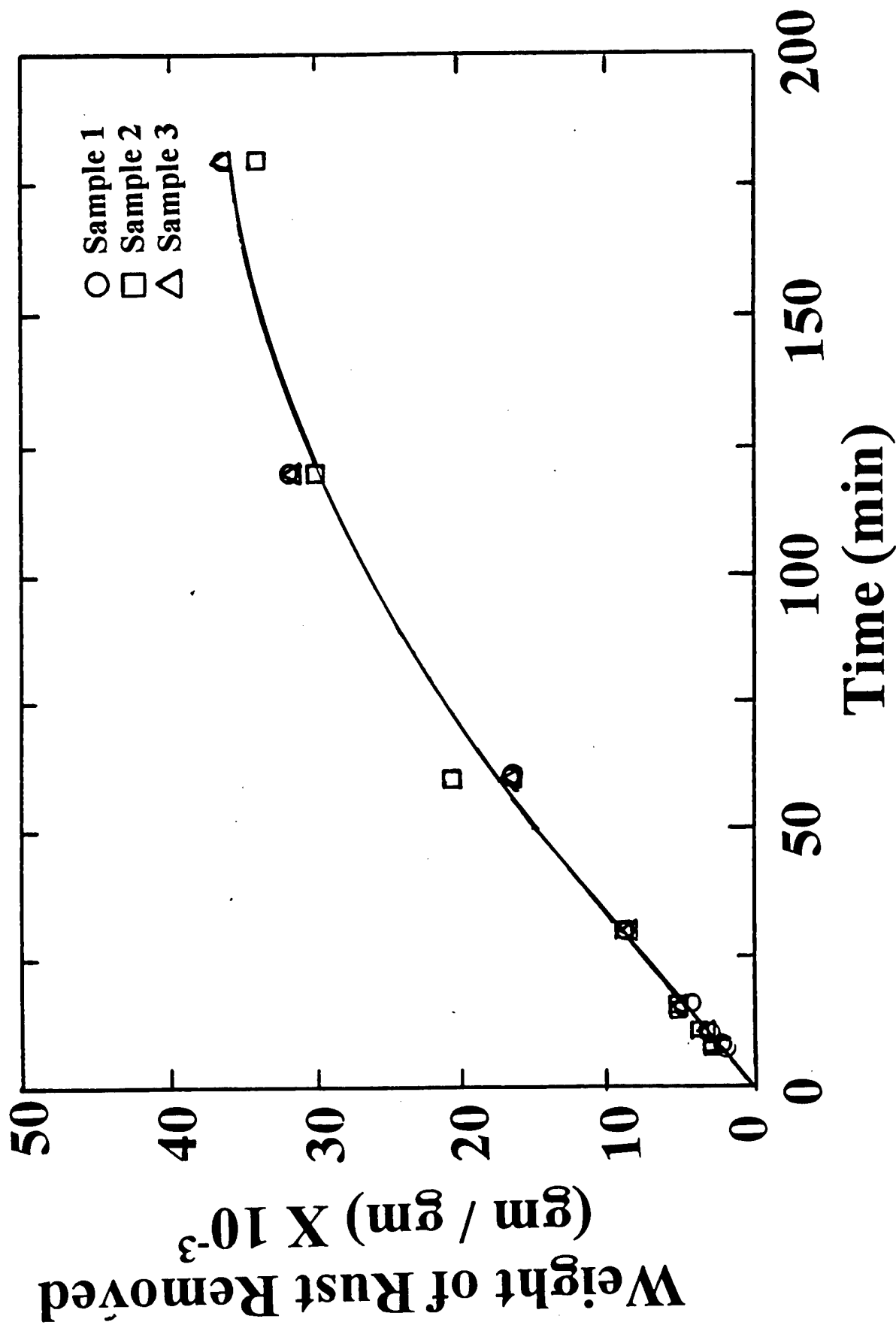


Figure 3. Weight loss versus time plot of 3 different heavily rusted steel samples in 2 vol % hydroxyethane diphosphonic acid solution at 27°C.

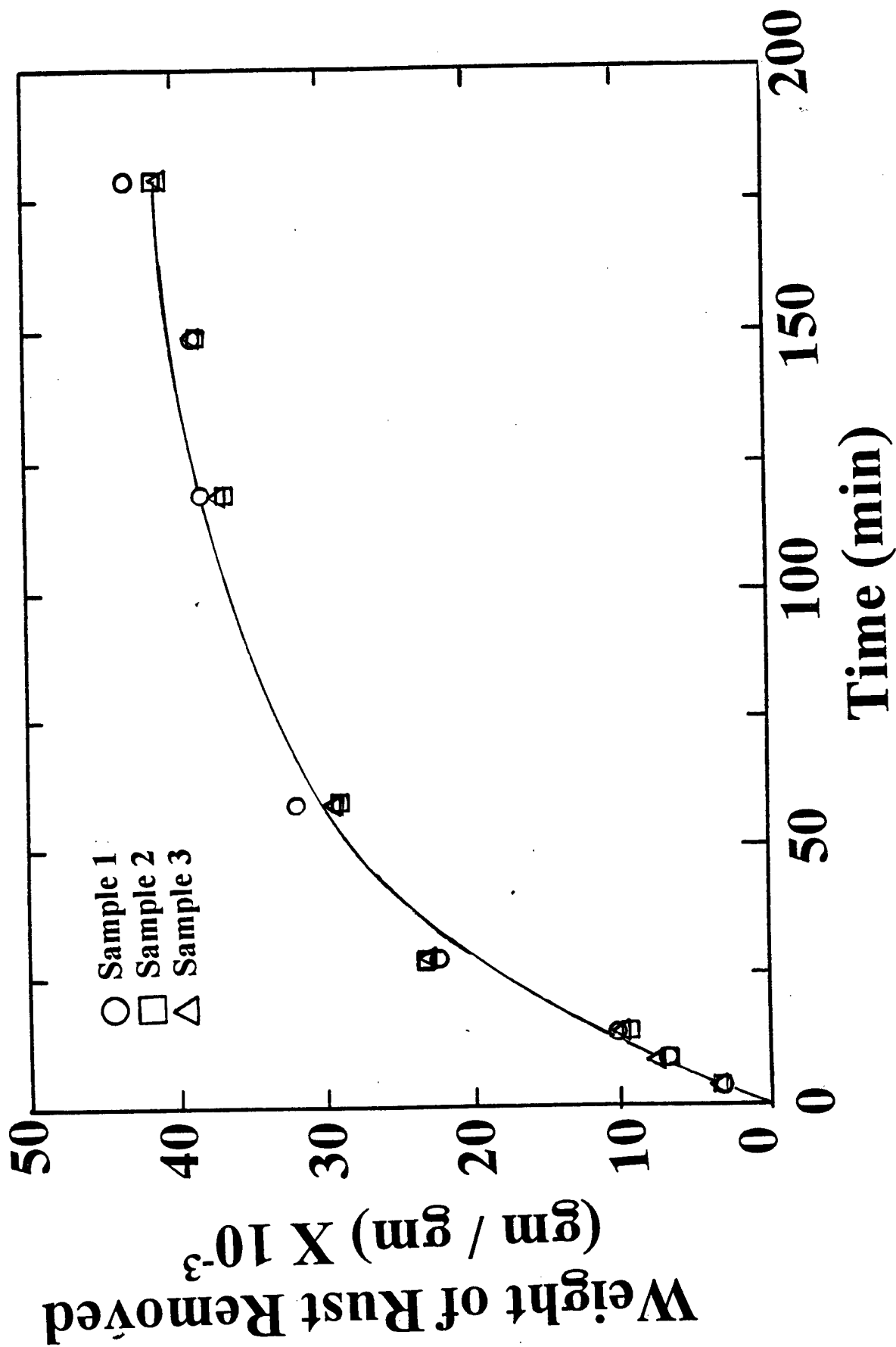


Figure 4. Weight loss versus time plot of 3 different heavily rusted steel samples in 2 vol % hydroxyethane diphosphonic acid solution at 40°C.

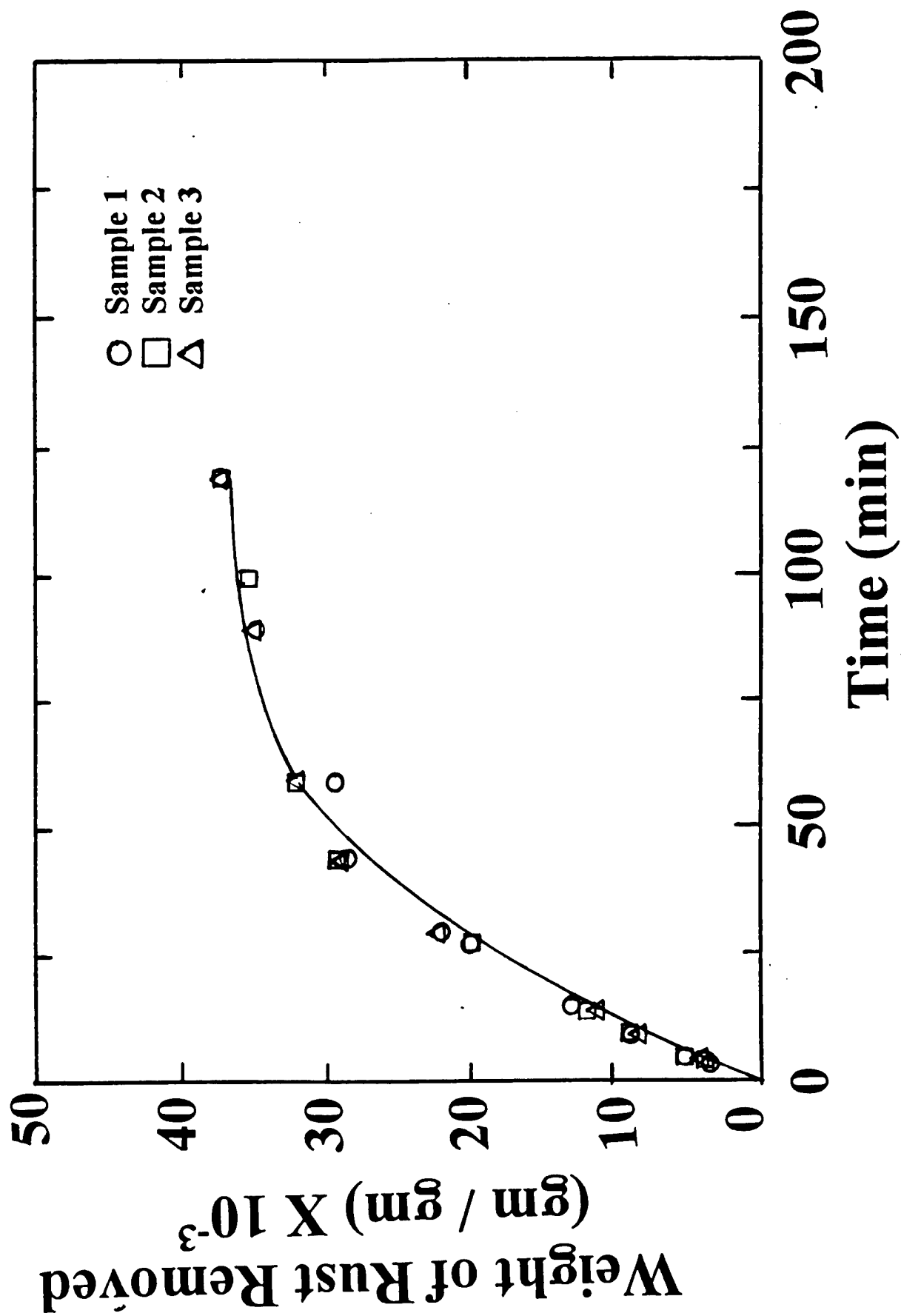


Figure 5. Weight loss versus time plot of 3 different heavily rusted steel samples in 2 vol % hydroxyethane diphosphonic acid solution at 50°C.

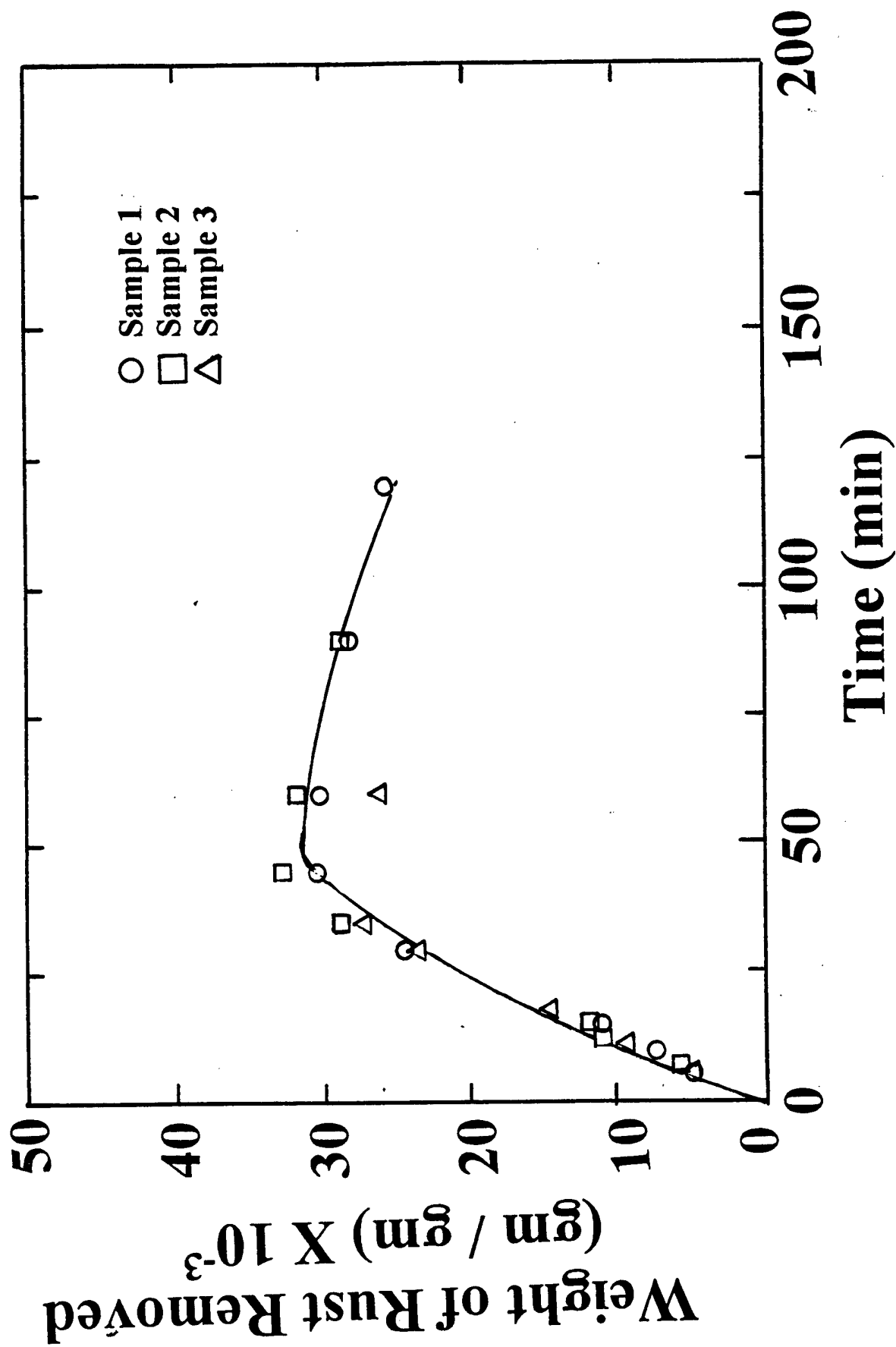


Figure 6. Weight loss versus time plot of 3 different heavily rusted steel sample in 2 vol % hydroxyethane diphosphonic acid solution at 60°C.

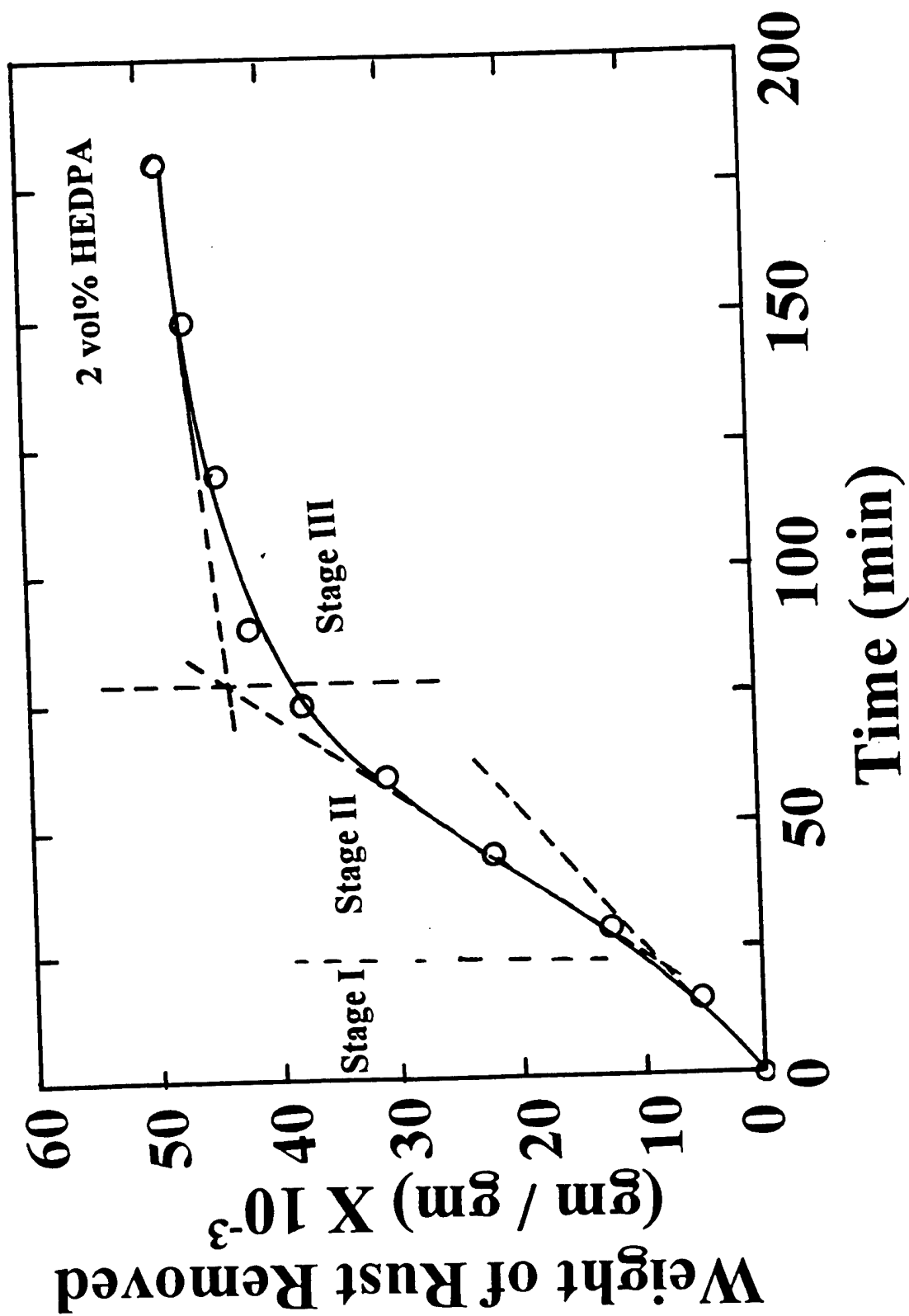


Figure 7. Weight loss versus time plot of heavily rusted steel sample in 2 vol % hydroxyethane diphosphonic acid solution at 27°C.

Table 1. Experimentally Determined Rate Constants for Rust Removal from Heavily Rusted Steel sample as a Function of Solution Temperature

Reaction Temperature (C)	Rate Constant (gm cm ⁻² min ⁻¹) X 10 ⁻³			
	Overall Process	Stage I	Stage II	Stage III
27	3.2	3.0	2.5	1.0
40	6.7	7.0	4.5	1.0
50	7.1	8.0	5.8	0.9
60	7.8	8.5	7.0	-3.0

Concentration of Hydroxy ethane diphosphonic acid (HEDPA) 0.082 M (2 vol%)
 Activation energy of the rust removal process : 11 ± 1 kcal/mole

The time for the termination of accelerated rust removal as a function of reaction temperature is given in Table 2, the order of reaction for different stages of the chemical process determined using the proposed model (given in the previous section). Table 3 shows the order of overall chemical reaction, and also the reaction processes.

The results suggest that with respect to the concentration of the oxide removal, the overall order of the reaction and the order of reaction in the first stage (only oxide is dissolved) is “first order”. The order of the reaction in the second stage where some oxide and mostly metal is removed is found to be 1.5 and the order of reaction in the third stage is found to be 3.5 respectively. However, the proposed model predicts that the order of reaction for stage II and stage III will be a “second order” (2) and “third order” (3) respectively.

The differences in the initially proposed model and the observed order of chemical reaction process can be explained as follows. The initially proposed model did not consider the chemical reaction independent of diffusion control. During the accelerated rust removal in the first stage, sample areas with very thin rust may expose the metal to the acid much sooner. Such sample heterogeneity induces the chemical reaction to progress via a diffusion process. Similarly, it is also possible that in the second stage, the oxide concentration is negligible compared to the metal concentration, hence, the order of reaction 1.5. The difference between the proposed and observed model during the third stage can be explained as follows. During Stage III, the model assumes that re-precipitation of one reaction product occurs. From the observed, the order of the reaction suggests that, in addition to the contribution by a diffusion controlled process (order 0.5), there are three additional active

Table 2. Time for the Termination of Accelerated Rust Removal and the Corresponding Chemical Kinetic Rate Constants as Function of HEDPA Acid Temperature

Solution Temperature (C)	T_i Time for the Termination of Accelerated Rust Removal Time (min)	Rate Constant (per min) X 10⁻²
27	113±10	4.3±0.7
40	53±10	11.5±2.5
50	41±4	13.0±0.5
60	36±2	13.5±0.2

Concentration of Hydroxy ethane di phosphonic acid (HEDPA) : 0.082 M (2 vol.%)

Sample Dimensions : ~ 4 cm diameter X 0.1 cm thick disks

Sample Weight : ~ 11 gm

No. of Samples Measured for Data Reproducibility : 9

Table 3. Order of Chemical Reaction For Each Stage of Chemical Transformation During Rust Removal from Heavily Rusted steel sample by 2 vol. % HEDPA Acid at Different Solution Temperatures.

Solution Temperature (C)	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	1.25 ± 0.2	1.00 ± 0.1	1.57 ± 0.25	4.00 ± 0.5
40	1.48 ± 0.2	1.30 ± 0.1	1.70 ± 0.25	2.70 ± 0.5
50	1.35 ± 0.2	1.20 ± 0.1	1.75 ± 0.25	3.50 ± 0.5
60	1.10 ± 0.2	1.00 ± 0.1	1.66 ± 0.25	3.00 ± 0.5

components (i.e. the concentration of three active species change with time) present in the chemical reaction.

In order to find some experimental support for the above postulated chemical processing, some analytical and structural analyses were conducted. Visually, it was observed that the sample rust is removed by 2 vol.% HEDPA solution at 25°C within 3 hours exposure. Gas (H_2 assumed) evolution was evident within 30 minutes. Continued exposure beyond the third hour resulted first in a gradual darkening of the surface and, then depending on the solution conditions, a relatively thick, white to cream colored precipitation formed sometime between 10 and 24 hours on the sample surface as well as in solution. At room temperature, this initial precipitation would re-dissolve within the next 24 hours resulting in a dark tea colored solution. A second precipitation would then occur during the third day's exposure. Figure 8 shows a visual characterization of the changes in the acid solution and precipitate formation on the surface of cleaned steel sample. Preliminary chemical analysis suggests that the solution, the precipitate in solution, and the precipitate on the cleaned sample surface contain a mixture of complex higher order phosphates of iron. Figure 9 shows a typical x-ray diffraction pattern obtained from a cleaned steel surface that became coated as a result of the re-precipitation of dark yellow precipitate after 48 hours of chemical treatment with 2 vol% HEDPA at 27°C. A casual examination of the HEDPA structure shows at least 5 sites for binding with Fe^{2+}/Fe^{3+} . Multiple complexing and rearrangements are considered possible. A systematic analysis of these chemical complexes of iron following x-ray diffraction and XPS analysis are in progress and the results will be included in the next report.

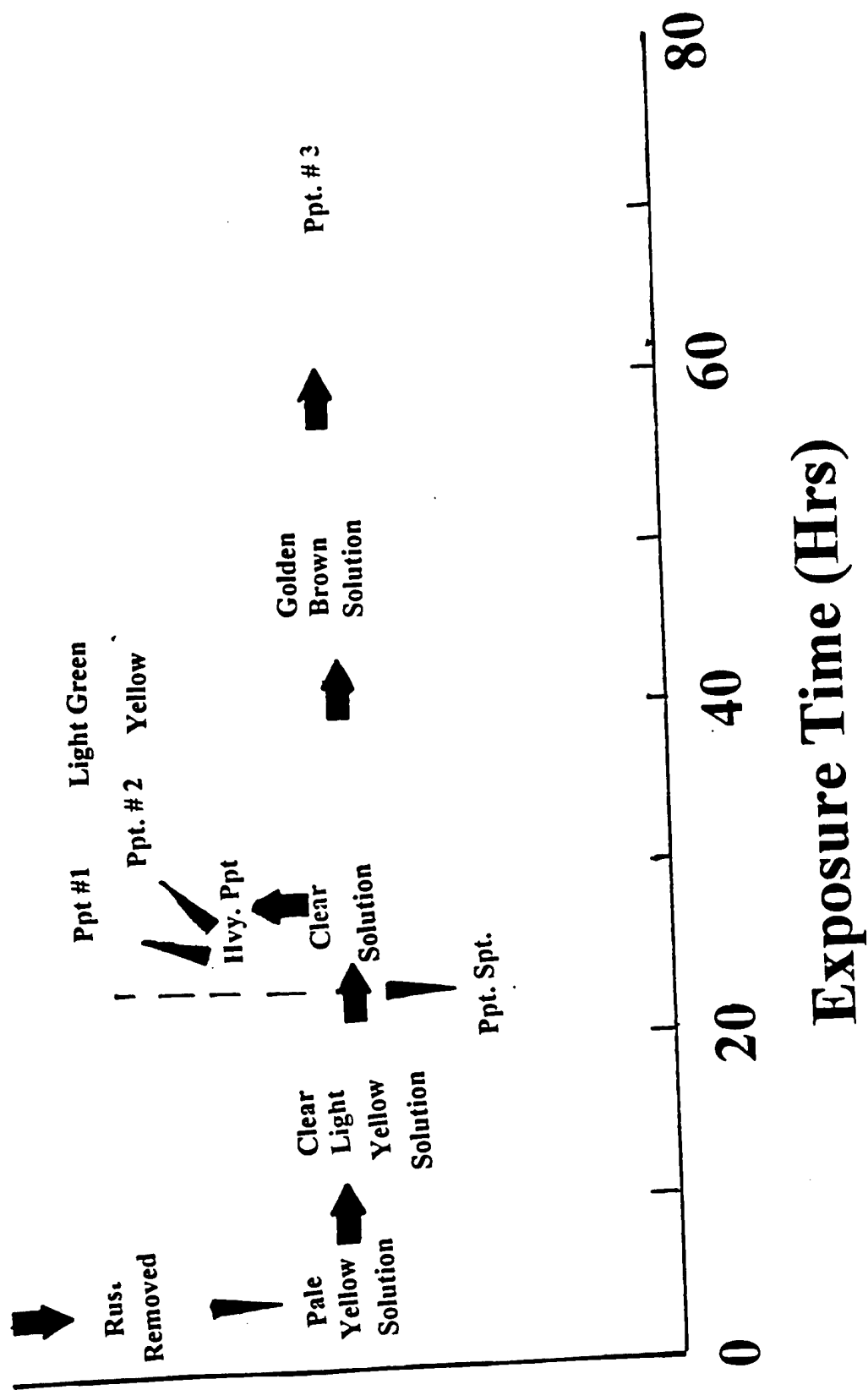


Figure 8. Visual characterization of sample surface and the solution phase during rust removal by 2 vol.% HEDPA acid at 27°C.

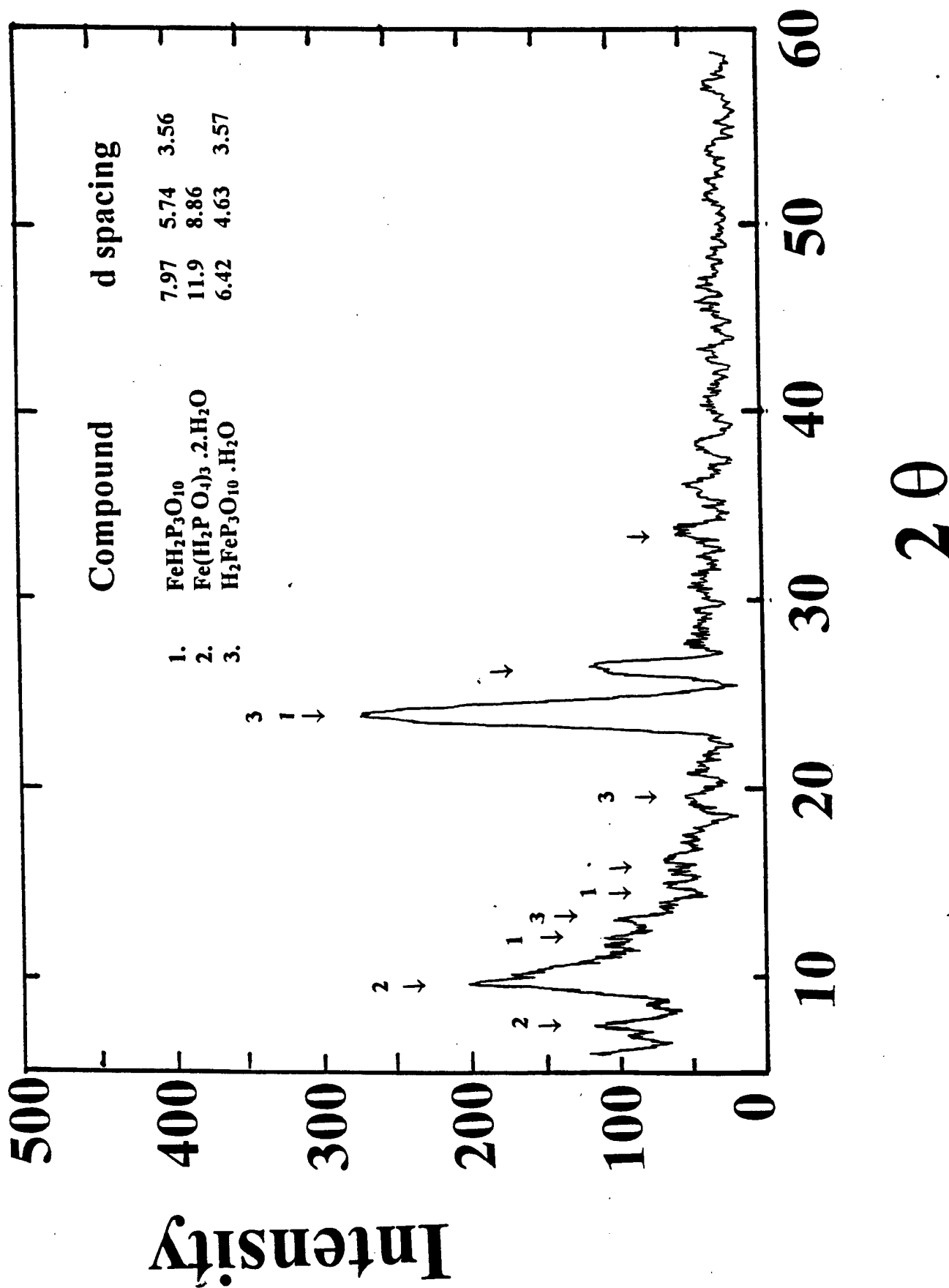


Figure 9. Typical x - ray diffraction obtained from cleaned steel sample coated with dark yellow precipitate (as a result of the re precipitation of reaction products) after 48 hours of chemical reaction with 2 vol.% HEDPA acid at 27°C.

Table 4. Maximum Time Required for complete Transition Between different Stages of Chemical Reaction represented as a Function of Solution Temperature

Reaction Temperature (C)	Time for Changes from Different Stages of the Reaction (hour)					
	Stage I		Stage I – II		Stage I – II – III	
	(Obs.)	Max. Calc.	Obs.	Max. Calc.	Obs.	Max. Calc.
27	2.5		48	60	72	100
40	2.0		18	21	36	72
50	1.25		12	24	24	63
60	0.5		2	21	3	14 (?)

Concentration of hydroxy ethane di phosphonic acid (HEDPA) 0.082 M (2 vol.%)

Stage I : Sample after rust - oxide is removed by HEDPA

Stage I – II : Sample has no oxide, metal is being removed and precipitate formed

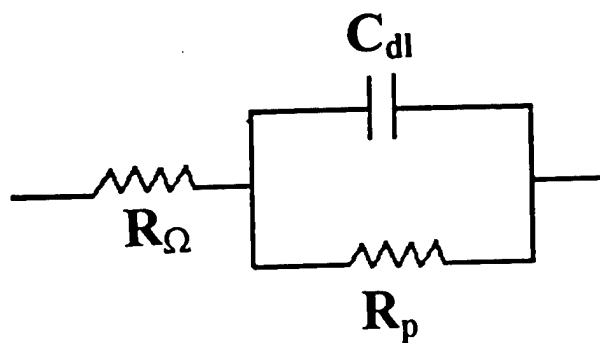
Stage I – II – III : Sample is covered with thick precipitate and / or precipitates

Obs : Visual observation during kinetic data measurement

Max. Calc. : Calculated using measured reaction rates. The theory assumes that the formation of precipitate goes through a maximum criticality for the completion of the process

An attempt was made to correlate the visual observation of the rust removal, precipitate adsorption, and its re-dissolution and re-precipitation with the theoretically calculated maximum time required for the completion of different stages of the reaction. The theoretical and visually observed results for the maximum times required for the completion of different stages of the chemical reaction are given in Table 4 as a function of solution temperature. These results did not show a good correlation between the theoretical and the experimental value. Although it can be argued that the differences are probably due to the theory assuming an absolute coverage at the molecular level, while the experimental are only the visual observations, the differences at higher reaction temperatures (in particular at 60°C) can not be ignored.

The electrochemistry of the steel/HEDPA surface reactions was followed for several experiments via electrochemical impedance spectroscopy (EIS), each run for a 72 + hour period. One initial question involved the quantity of steel surface area that could be cleaned by a given volume of HEDPA. As noted earlier, the conventional simplified Randles Circuit model (Figure 10) could be used to analyze the electrode behavior for the majority of the EIS runs. Typical Bode Magnitude plots taken at intervals during the 73 hour exposure of the steel with a somewhat limited quantity of HEDPA are presented in Figure 11. The low impedance values for the first 10 hours indicate a reasonable high rate of dissolution of the steel in the HEDPA solution. The shift to higher impedance values at the 23 hour exposure shows the decrease in the steel dissolution rate when the initial precipitation occurs in the bulk solution. The increase in impedance at the second day holding into the third day suggests a passivation of the steel surface has occurred.



Where:

R_{Ω} = Bulk Solution Resistance

R_p = Polarization Resistance of Metal Reaction

C_{dl} = Metal Interfacial Double – Layer capacitance

Figure 10. Simplified Randles equivalent circuit model for metal – solution reactions

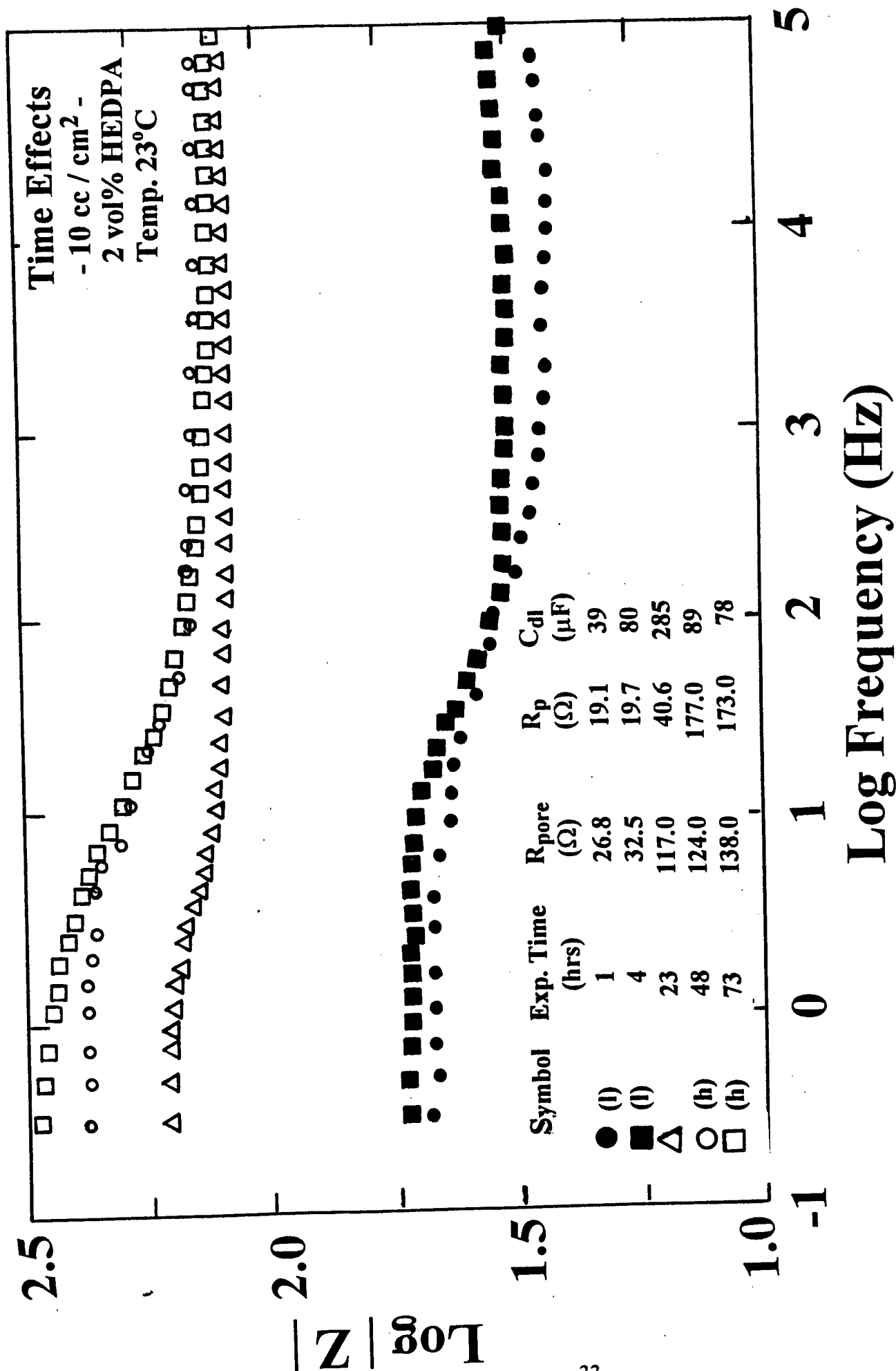
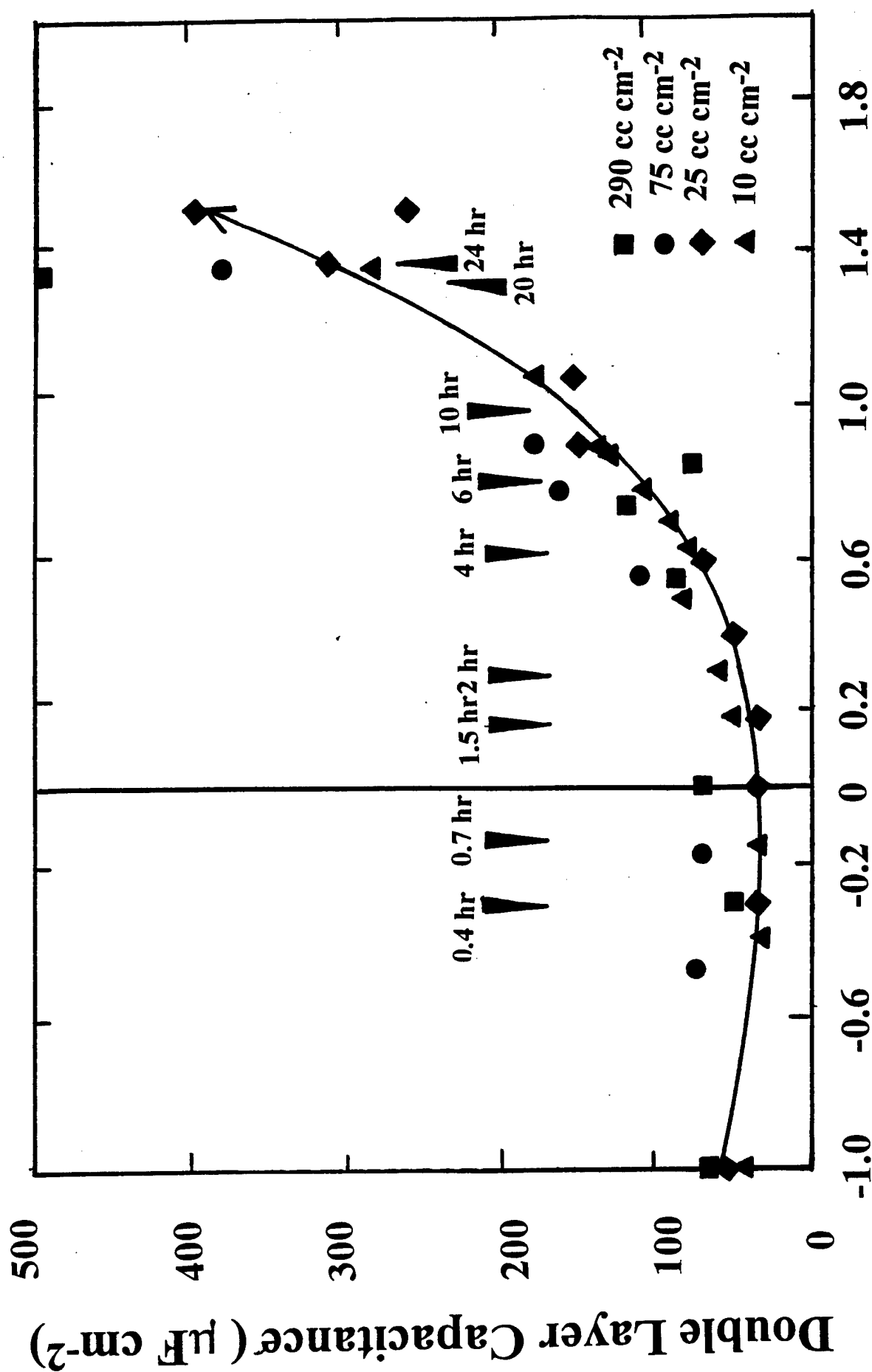


Figure 11. Bode magnitude plots for steel - 2 vol. % HEDPA solution at 23°C as a function

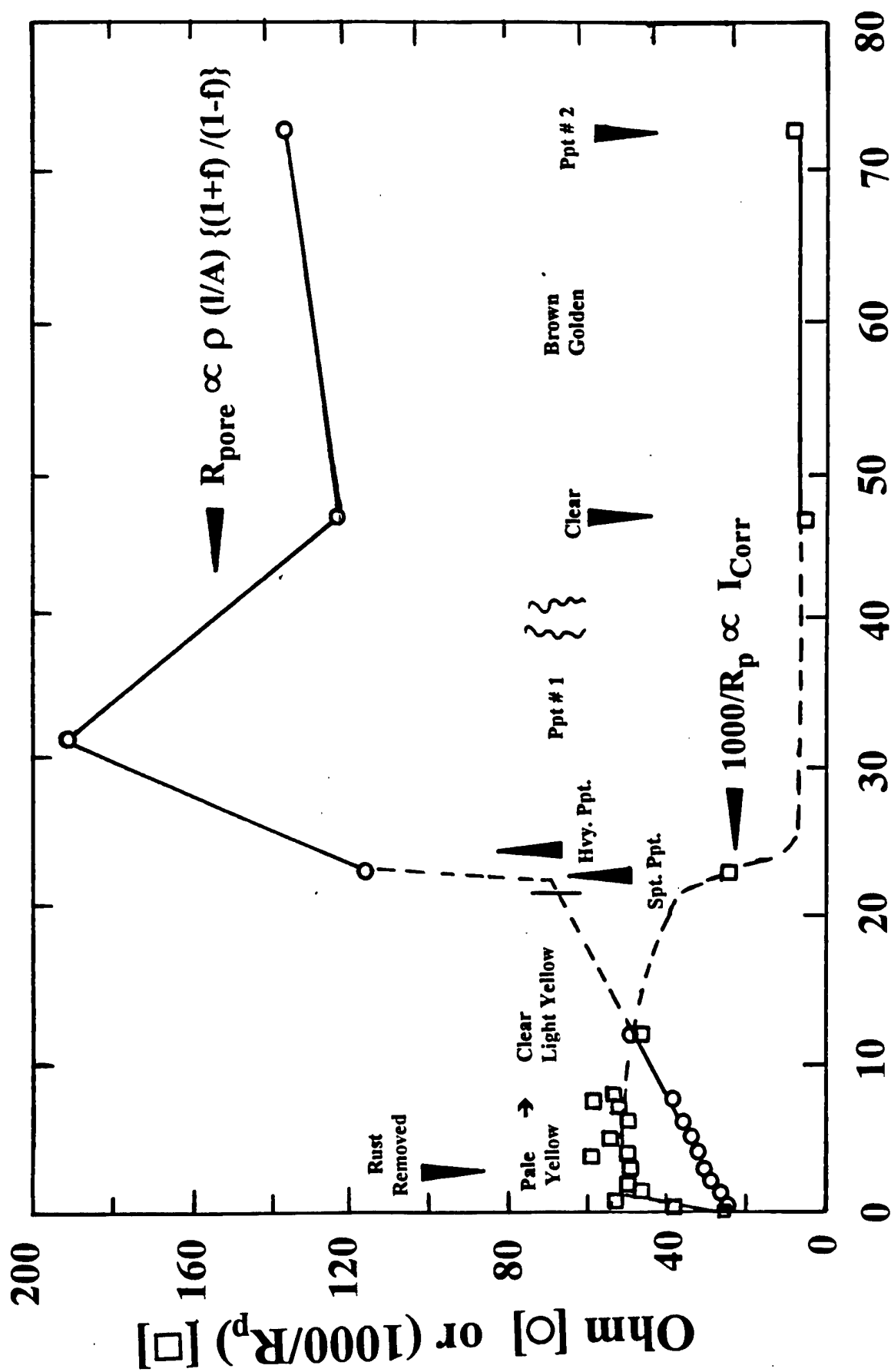
As seen in Figure 12, the initial double layer (C_{dl}) value of approximately $50 \mu\text{F}/\text{cm}^2$ calculated from EIS data using the model shown in Figure 10 was found to decrease to $25 \mu\text{F}/\text{cm}^2$ in approximately one hour, (the $25 \mu\text{F}/\text{cm}^2$ C_{dl} value being the "classical value" appropriate for a bare metal surface in an aqueous electrolyte). The minimum occurred at approximately the same time-of-exposure for the different liquid volume to metal surface area ratios as one might expect. The following time dependent increase of C_{dl} would suggest a combination of some surface roughening and the start of a deposition of a surface coating.

One initial claim by the ANL personnel was that HEDPA removed the rust from a rusty steel surface and passivated the cleaned surface. However, the EIS determined R_p values (plotted in Figure 13 as $1000R_p^{-1}$) indicates that the metal dissolution process is high and continues even after the oxide surface has been removed. As seen in the figure, the R_p values remain about the same from the 1 hour point (where the steel surface was at a minimal C_{dl}) until the 10th hour, when the last EIS run was made that day. (Typical steel R_p values for neutral pH electrolytes are in the range of $2 \times 10^3 \Omega \cdot \text{cm}^2$.) There is some uncertainty as to the exact time that a 2 fold decrease in steel dissolution occurred but the observed change by the 24th hour may correspond to the observation of the precipitate in solution. A second lowering occurred by the 48th hour of exposure when the bulk precipitate had dissolved. At this point the reagent could be considered to have passivated the steel surface. However, the pore impedance (R_{pore}) increase during these same events suggests the ionic conductivity component from the reagent has decreased significantly, possibly the effect of complexing association with the $\text{Fe}_{+2}/\text{Fe}_{+3}$ ion(s). In that the increase of the R_{pore} values can reflect both



Log Exposure Time (Hrs)

Figure 12. Effect of 2 vol.% HEDPA acid on the double layer capacitance of steel surface as a function of continuing exposure time.



Exposure Time (Hour)

Figure 13. Time dependent changes to the pore resistance (R_{pore}) and R_p for steel during the steel sample surface exposure to 2 vol.% HEDPA at 23°C.

the presence and changes to a coating appearing on the steel surface as well as a lowering of the solution conductivity within the porous coating, an independent determination of the solution conductivity would appear to be warranted in any future runs.

The metallic dissolution rate (prior to any passivation) should exhibit 1st order kinetics with respect to HEDPA up to a given concentration and then should show no further increase. The five EIS experiments did allow an approximation determination of this behavior even though the runs should have been controlled to a greater degree with respect to the solution temperature and stirring rate. The HEDPA consumption was assumed to be proportional to the corrosion current as recalculated from the R_p values determined via the EIS runs. This "consumption" was then subtracted from the initial HEDPA concentration resulting in a calculated "free HEDPA" concentration. The specific calculated currents for the four experiments with the solution stirred between the EIS runs are then plotted against the "free HEDPA" as shown in Figure 14. The data appear to follow the expected behavior in general terms and the data suggest a constant corrosion rate above 1.5 v/o (0.06 M) HEDPA. A similar plot can be shown for the reciprocal R_{pore} values versus "free HEDPA" concentrations, although there is no concentration limit.

The stirring rate effects can be seen in the tabulated data from two different exposure times during the 4th run. The effect was demonstrated several times by having the stirrer either on or off during the EIS determination. The tabulated corrosion rates ($\mu A/cm^2$) calculated from the R_p values are listed in the order taken. The lowering in the corrosion rates with exposure time is the effect of less "free HEDPA" as shown previously in Figure 14.

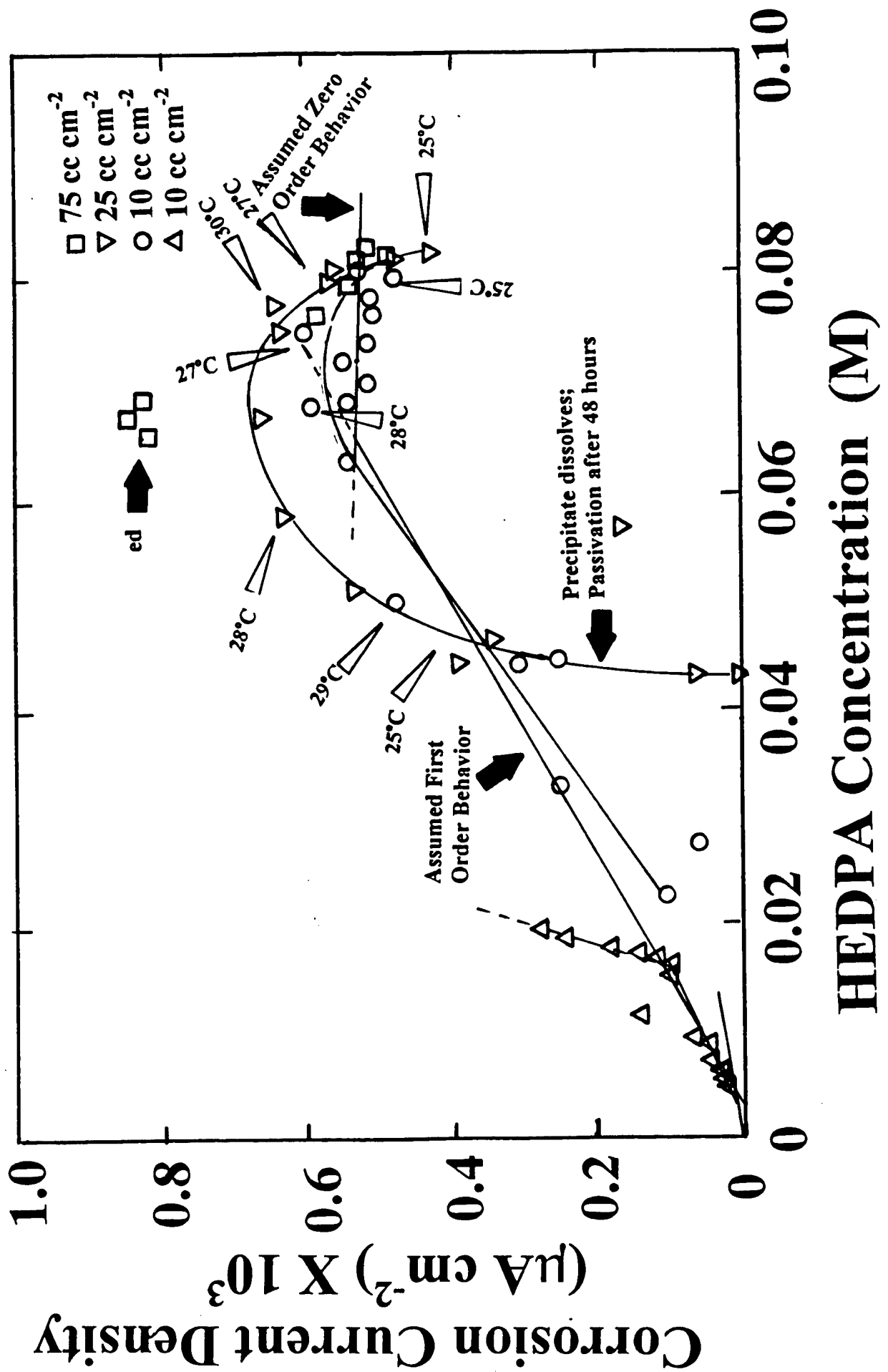


Figure 14. Calculated steel corrosion resistance ($\mu\text{A cm}^{-2}$) represented as a function of "free HEDPA" concentration at 27°C

During the first 2 hours exposure, when the HEDPA concentration is sufficient, the effect of stirring rate appears to be negligible (Table 5).

SUMMARY AND CONCLUSION

The preliminary studies concur with the oxide removal effectiveness of HEDPA with rusted steel. At the levels of HEDPA concentration used in the study, the oxide removal kinetics were found to be activation controlled - with an activation energy of 11 kcal/mole Fe. With a smooth steel surface the C_{d1} measurements indicate the air formed oxide film is removed at approximately one hour exposure. The R_p values indicate the parent metal is also significantly attacked by the reagent while a surface film continues to build with increasing exposure time. This film does not retard the substrate corrosion process while sufficient HEDPA reagent is available. Additional exposure time allows the formation of a precipitate both on the sample surface and in solution after 24 hour exposure. The precipitate subsequently dissolves with additional exposure and re-precipitates within the 72 hours tested to date. Further work is planned to identify the chemistry of the precipitates as well as determine the suitability of the coated surface for an adherent organic coating.

Table 5. Corrosion rate versus exposure time as a function of stir number for steel samples immersed in 2 vol.% Hydroxy ethane diphosphonic acid at 27°C

Stir Number	Corrosion Rate ($\mu\text{A cm}^{-2}$)	
	Exposure Time	
	7-8 Hours	23 – 24 Hours
0	930	425
3	930	523
6	1015	523

ACKNOWLEDGEMENT

This research effort was funded under Office of the Naval Research 6.1 ILIR research effort program at the Naval Surface Warfare Center Craderock Division managed by Dr. B.E. Douglas. The authors thank Albright & Wilson (A&W) for the supply of HEDPA and Mr. J. Tabor (A&W) for providing several appropriate technical articles. The authors also appreciate the discussions and suggestions from colleagues at the DOE's Argonne National Laboratory, Drs. E.P. Horowitz, A. Purohit and K.L. Nash for strong assistance during the initial programmatic evaluation of the project.

REFERENCES

1. Chiarizia, R. and E.P. Horowitz, *Hydrometallurgy*, 27, 339-360, 1991
2. Horowitz, E. P., Diamond, H., Gatrone, R. C., Nash, K. L. and Rickett, P. G., "Solvent Extraction," ed. T. Sekine, Pub. Elsevier Science, 1992.
3. Nash, K. L., *Radiochemica*, 54, 171-179, 1991
4. Partridge, P. E., "Adaptability of Pipeline Decontaminated Procedures to Real Industry," P/N 98621, *Corrosion* 98, NACE Intl. Houston, TX, 1998.
5. Graedel, T.E. and R.P. Frankenthal; "Corrosion Mechanisms for Iron and Low Alloy Steels Exposed to the Atmosphere", *J. ECS*, 137, No. 8, pp 2385-2394, August 1990.
6. Surana, V. S. and Warren, H. J., *Trans. Inst. Min. Metallrg. Society*, C 28, 133-139, 1969.
7. Warren, I. H. and Devuyt, W., "Leaching of Metal Oxides," *Proc. Int. Symp. On Hydrometallurgy*, Pub. AIME, 229-264 (1973)
8. Cornell, R. M., Posner, A. M. and Quirk, J. P., *J. Inorg. Nucl. Chem.*, 38, 563, 1976.
9. Osseo-Asare, K., "Interfacial Phenomena in Leaching Systems," *Hydrometallurgical Process Fundamentals*, ed. R. G. Bautista, Plenum Pub., New York, 227-268, 1982.
10. Nicol, M. J., "The Non-Oxidative Leaching of Oxides and Sulfides: An Electrochemical Approach," *Hydrometallurgy Research, Development and Practice*, eds. K. Osseo-Asare and J. D. Miller, Pub. AIME, New York, 177-195, 1982.
11. Diggle, J. W., "Dissolution of Oxide Phases," *Oxides and Oxide Films*, ed. J. W. Diggle, Pub. Marcel and Dekker, Vol. 2, 281-386, 1973.
12. Murray, J.N., P.J. Moran and E. Gileadi: "Utilization of Specific Pseudo Capacitance for the Determination of the Area Corroding Steel Surfaces", *Corrosion*, 44 No. 8, pp 533-538, 1988.

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